

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Vat Dyeing

5 We, CELANESE CORPORATION OF AMERICA, of 180, Madison Avenue, New York, 16, New York, United States of America, a company incorporated in accordance with the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to the dyeing of textile materials containing cellulose acetate or another organic derivative of cellulose, and more particularly to the dyeing of textile fabrics of cellulose acetate with vat dyestuffs.

15 Vat dyes are largely applied to cellulose textile materials, for example, cotton, by first reducing or vatting the dyestuff in water by treatment with a reducing agent, such as sodium hydrosulphite, and an alkaline material, such as sodium hydroxide, to produce an aqueous solution of the soluble salt of the leuco or reduced form of the vat dyestuff and applying

20 this solution to the textile material, which is then subjected to oxidising conditions, for instance exposure to air, to convert the leuco salt into the oxidised insoluble form of the dyestuff.

30 However, this method is not of general application for applying vat dyes to textile materials containing cellulose acetate; little or no dyeing may take place and/or the cellulose acetate may be undesirably saponified by the alkaline dye baths. By the addition of an acid, for example, acetic acid, the aqueous solution of the soluble salt of the leuco form of a vat dyestuff, particularly if it contains a dispersing agent, may be converted into an aqueous dispersion of the vat acid, i.e. the free leuco compound; by using such dispersions a considerably wider range of vat dyes may be applied to cellulose acetate. Nevertheless, even when employed as such aqueous dispersions, many

40 vat dyes yield poor dyeings on textile materials containing cellulose acetate or other organic derivatives of cellulose; the dyeings being unlevel, unreproducible, of poor colour value, and showing heavy crocking. Poor dyeing results even though the vat acid dispersions

used are clear, extremely fine and stable, show no precipitation on standing, and give perfect tests on filter paper. It appears that the poor results are due to the fact that the dye is deposited at the surface of the fibre in one 55 form or another and does not penetrate adequately into the fibres of the cellulose acetate or other organic derivative of cellulose even in the presence of a swelling agent.

According to the present invention textile 60 materials containing cellulose acetate or another organic derivative of cellulose are coloured with a vat dye by applying to the textile material the vat dye as an aqueous dispersion of the vat acid, the dispersion containing poly- 65 vinyl pyrrolidone, and oxidising the vat acid to the parent vat dye on the textile material. In this way it has been found possible to secure good penetration of the vat acids of a wide range of vat dyes into cellulose acetate and to obtain dyeings which show practically no 70 crocking and are level, readily reproducible and of good colour value.

The process of this invention will be more particularly described with reference to textile 75 materials containing cellulose acetate, although the process is also applicable to textile materials containing other organic derivatives of cellulose.

The results obtained by the use of the com- 80 bination of the dispersed vat acid and the polyvinyl pyrrolidone are very surprising in view of the known effects of polyvinyl pyrrolidone when vat dyeing cotton or regenerated cellulose materials. In the processing of such 85 materials polyvinyl pyrrolidone is used as a stripping agent, in the presence of an alkaline reducing agent, to remove the vat dye from the cotton or regenerated cellulose fibres. It has been postulated in the prior art that this strip- 90 ping action is due to a very powerful attraction between the dyestuff and the polyvinyl pyrrolidone, the bond between the dyestuff and the polyvinyl pyrrolidone being much stronger than the attraction 95 of the cellulose for the dyestuff. The prior art has recognised that this powerful bond between the dyestuff and the polyvinyl pyrrolidone in the alkaline vat dye bath obviously operates against its use as levelling assistant in the vat 100

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dye bath, so that the polyvinyl pyrrolidone has been used in levelling only finished vat dyeings which are uneven, in which case it operates because of its stripping action.

- 5 By the use of the process of the present invention excellent dyeings have been obtained with a large number of vat dyestuffs, including dyes of the indigoid, thioindigoid, violanthrone, pyanthrone and indanthrone types.
- 10 Among the many vat dyes which have been tried with excellent results are Jade Green C.I. 1101; Helindon Brilliant Blue 4B C.I. 1184; Ahcovat Golden Yellow GK Pr. 291; Ahcovat Brilliant Violet 4R C.I. 1104; Calcosol Violet 6RD C.I. 1212; Ahcovat Orange RKS; Calcosol Fast Yellow; Indanthrene Brilliant Yellow 3G; Ahcovat Yellow 4GS; Calcosol Pink FFD Pr. 109.

- 20 Preferably the concentration of polyvinyl pyrrolidone employed in the dispersion should be between about 0.2 and 2 grams per litre.

- The aqueous dispersion of the vat acid may be made, for example, by solubilising the vat dyestuff by reducing it to the leuco form in an aqueous alkaline medium, followed by the addition of acid, for example acetic acid, in the presence of polyvinyl pyrrolidone. If desired, the resulting vat acid dispersion may be oxidised to produce a dispersion of the oxidised dyestuff, which dispersion may be stored for a considerable period of time and then directly reduced, when needed, into a dispersion of the vat acid by using, for example, zinc sulphonylate formaldehyde.

- 35 It is desirable, particularly when darker shades are required, to have present a swelling agent for cellulose acetate. Swelling agents, for example 2-butoxy ethanol and the monobutylether of diethylene glycol (2-butoxyethoxy ethanol), diacetone alcohol and triethyl phosphate, may be present. The concentration of swelling agent should preferably be below that which causes delustering of cellulose acetate. The swelling agent may be added at any stage of the preparation of the mixture, but is preferably added to the vat acid dispersion rather than to the alkaline vatted mixture.

- The dyeing process may be carried out using a wide range of temperatures. Preferably however, the dye bath is maintained at a temperature in the range of 70° to 95° C.

- The dispersion of the vat acid containing polyvinyl pyrrolidone is preferably applied to the textile material at a pH of 4 to 7, e.g. 5 to 7. Preferably acetic acid should be used to liberate the vat acid. Other suitable acids are, for example, formic, oxalic, and citric acids.

- The dispersion of the vat acid may also be made with the aid of an amine, for example, hexamethylene diamine, cyclohexylamine, pyrrolidine or ethylene diamine. For example, the vat dye may be vatted with a reducing agent, e.g. sodium hydrosulphite, in water in the presence of the amine. The concentration

of the amine should be such that the pH of the dispersion is not above 7, preferably 6—7, or the pH value of the resulting dispersion should subsequently be adjusted to below 7.

In order to maintain the dispersed vat acid in the reduced state a reducing agent should be present. Preferably, this reducing agent should be one which will prevent the vat acid from oxidising in a slightly acid dye bath over an extended period of time at an elevated temperature. Particularly desirable reducing agents for this purpose are zinc sulphonylate formaldehyde  $\text{Zn}(\text{HSO}_2\text{CH}_2\text{O})_2$  and sodium sulphonylate formaldehyde  $\text{NaHSO}_2\text{CH}_2\text{O}$ , e.g. "Hydrosulphite AW", especially if used in a dispersion maintained at a pH of 4—6, and thiourea dioxide which is most suitable in a dispersion maintained at a pH above 6. Sodium hydrosulphite effects rapid reduction of the vat acid but does not maintain the dye bath in a reduced condition for a long time at a pH much below 7.

After the fabric leaves the dye bath, it may be rinsed and then oxidised. Any suitable oxidising medium may be employed, for example hydrogen peroxide, sodium perborate or sodium nitrite acidified with sulphuric acid. The addition of a swelling agent to the oxidising agent assists the oxidation. A hot soaping treatment is frequently advantageous in order to ensure that the shade of the dye is properly developed. A steaming treatment may be employed for this purpose in place of or in addition to the hot soaping treatment. A steaming treatment may be applied before the oxidation if desired.

The dispersion of the vat acid may be applied, if desired, by mechanical impregnation as by pad dyeing or printing. For such applications, the dispersion may be thickened in any convenient way, for example with a gum, such as gum tragacanth, or a water-soluble alkyl cellulose, e.g. methyl cellulose or hydroxyethyl cellulose. Following the impregnation, the material may be dried, steamed, under pressure if desired, washed and oxidised.

In order further to illustrate the present invention, the following examples are given:—

#### EXAMPLE 1.

2.00 parts by weight of Jade Green C.I. 1101, (12:12'-dimethoxy dibenzanthrone), were dispersed, by stirring, in 1000 parts by weight of water containing 5 parts by weight of "Peregal ST" (Peregal is a Registered Trade Mark), which is a 30% solution of polyvinyl pyrrolidone in water, having a specific gravity of about 1.04. Then 22 parts by weight of a 10% solution of sodium hydroxide in water and 2 parts by weight of sodium hydrosulphite were added and the mixture was heated to 50—60° C. and 10—15 minutes to completely reduce the dye to the sodium leuco compound. To the resulting mixture were added rapidly, with stirring, 4000 parts by

weight of water containing 3 parts by weight of glacial acetic acid. This formed a dispersion of the vat acid. 10 parts by weight of zinc sulphoxylate formaldehyde  $Zn(HSO_3, CH_2O)_2$  and 90 parts by weight of 2-butoxy ethanol were added to the filtered dispersion, to produce a dyebath having a pH in the range of 4.5—5.5. This dyebath was heated to 80—85° C. and agitated. 100 parts by weight of cellulose acetate textile fabric were immersed in the hot agitated dyebath for 2 hours, after which the dyed fabric was rinsed in lukewarm water and oxidised by immersion in an aqueous bath containing 5 grams per litre of sodium perborate. After oxidation, the dyed fabric was soaped for 20 minutes at 70—80° C. with an aqueous solution containing 1.5 grams per litre of green soap. The fabric was coloured a full, level, bluish-green shade, which showed practically no crocking, and had a good hand.

#### EXAMPLE 2.

Example 1 was repeated except that Calcosol Pink FFD Pr. 109 was substituted for the Jade Green dyestuff. The dyed fabric was coloured a full, level pink shade, which showed practically no crocking and which had good light fastness.

#### EXAMPLE 3.

Example 1 was repeated except that the 90 parts of 2-butoxy ethanol were replaced by 65 parts of diethylene glycol monobutyl ether. Similar excellent results were obtained.

#### EXAMPLE 4.

Example 1 was repeated, except that the 2-butoxy ethanol was omitted. The fabric was coloured a medium, level, bluish-green shade which showed practically no crocking.

#### EXAMPLE 5.

A dyebath was prepared from 0.4 gram per litre of Jade Green C.I. 1101, 1 gram per litre of Peregal ST, 1 gram per litre of hexamethylene diamine, and 2 grams per litre of sodium hydrosulphite by adding the vat dye to the aqueous solution containing the Peregal ST and hexamethylene diamine, at 40° C., and then adding the sodium hydrosulphite and effecting reduction by heating to 80° C. 500 parts of this dyebath, the pH of which was adjusted to 6.5 to 7, were used to dye 10 parts by weight of cellulose acetate textile fabric for two hours at 80° C. while agitating the dyebath, after which the dyed fabric was rinsed in lukewarm water and oxidised by sodium perborate. After oxidation, the dyed fabric was soaped. The fabric was coloured a medium, level, bluish-green shade, which had a neat appearance, showed practically no crocking and had a good hand.

#### EXAMPLE 6.

Example 5 was repeated with the exception that the dyebath also contained butoxyethanol,

at a concentration of 10 cc. per litre. The dyed fabric was similar to that described in Example 5 but had a pronouncedly heavier shade.

The process described in Example 1 was repeated with the exception that in place of the Peregal ST there was substituted one of the following dispersing agents: (a) "Tamol N" a sodium salt of a condensed aryl sulphonic acid, made by condensing naphthalene sulphonic acid with formaldehyde; (b) "Dispersol VL" (Dispersol is a Registered Trade Mark), a condensation product of ethylene oxide and a long chain fatty alcohol, of (c) "Sandopan TN" a synergistic mixture of anionic and non-ionic compounds. In each case the vat acid dispersion was fine, clear and stable. When a drop of each dispersion was placed on filter paper and allowed to spread through the paper, the outside of the ring formed by the spreading dyestuff had the same shade as the centre, where the drop was originally placed. However, the dyeings on cellulose acetate using these dispersing agents were poor in that they were not level, not reproducible, and showed heavy crocking. The dyestuff formed a layer on the fibre surface. The same results were obtained when the concentration of each dispersing agent was increased fourfold.

The process described in Example 1 was repeated with the exception that in place of the Peregal ST there was substituted one of the following dispersing agents: (d) "Triton X-100" (Triton is a Registered Trade Mark), an alkyl aryl polyether alcohol; (e) "Tinegal CV" a quaternary ammonium compound; (f) "Nonisol-100" a polyoxyalkylene ester. In each case the vat acid dispersion was fine, clear, and stable and gave perfect results when tested on filter paper in the manner described above. The dyeing on cellulose acetate in the dyebath appeared to be very heavy. However, on rinsing in luke-warm water the dyestuff was removed almost completely from the fibre in each case. The same results were obtained when the concentration of each of these dispersing agents was increased fourfold.

The processes described in the two paragraphs immediately preceding were repeated except that Calcosol Pink FFD was substituted for the Jade Green. The use of this dye did not in any way improve the results described.

While we have disclosed the process of the present invention with particular reference to the colouring of textile materials containing cellulose acetate fibres, the process is equally applicable to the colouring of other materials which have a basis of other organic derivatives of cellulose. Examples of such other organic derivative of cellulose are cellulose esters, for example cellulose propionate, cellulose butyrate, cellulose acetate propionate and cellulose acetate butyrate and cellulose ethers for example ethyl cellulose and benzyl cellulose. The process can be applied to the organic derivatives of cellulose in the form of con-

tinuous filament yarns, or fabrics containing these yarns, staple fibre products for example loose staple fibre, rovings, yarns or fabrics, or to self-supporting films.

5 What we claim is:—

1. Process for the colouration of textile materials containing an organic derivative of cellulose with a vat dye, which comprises applying to the textile material the vat dye as an aqueous dispersion of the vat acid, the dispersion containing polyvinyl pyrrolidone, and oxidising the vat acid to the parent vat dye on the textile material.

2. Process for the colouration of textile materials containing cellulose acetate with a vat dye, which comprises applying to the textile material the vat dye as an aqueous dispersion of the vat acid, the dispersion containing polyvinyl pyrrolidone, and oxidising the vat acid to the parent vat dye on the textile material.

3. Process according to Claim 1 or 2, wherein the textile material is immersed in the aqueous dispersion and is allowed to take up the vat acid which is then oxidised to the parent vat dye on the material.

4. Process according to any of the preceding claims, wherein the aqueous dispersion has a pH of 4 to 7.

5. Process according to any of the preceding claims, wherein the aqueous dispersion contains a swelling agent for the organic derivative of cellulose.

6. Process according to Claim 5, wherein the swelling agent is 2-butoxy-ethanol or 2-butoxyethoxy-ethanol.

7. Process according to any of the preceding claims, wherein the aqueous dispersion contains a reducing agent.

8. Process according to Claim 7, wherein the dispersion contains zinc sulfoxylate formaldehyde or sodium sulfoxylate formaldehyde as a reducing agent.

9. Process according to any of the preceding claims, wherein the temperature of the aqueous dispersion is 70° to 95° C.

10. Process according to any of the preceding claims, wherein the vat dye is 12:12'-dimethoxy-dibenzanthrone.

11. Process for dyeing textile materials containing cellulose acetate or another organic derivative of cellulose with a dispersion of a vat acid, the dispersion containing polyvinyl pyrrolidone, substantially as described.

12. Process for dyeing textile materials containing cellulose acetate with a dispersion of a vat acid, substantially as described in the examples.

13. An aqueous dispersion of a vat dye in the form of the vat acid, the dispersion containing polyvinyl pyrrolidone.

14. An aqueous dispersion of a vat dye in the form of the vat acid, the dispersion containing polyvinyl pyrrolidone and having a pH of 4 to 7.

ALLEN & BUTTERWORTH,  
Chartered Patent Agents,

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